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(54) Title: METHOD OF MANUFACTURING GLASS-CERAMIC ARTICLES

(57) Abstract

Glass ceramic articles of a defined shape, particularly thin products and products with sharp corners, are made by forming the shape of the desired article from a mixture of powdered glass particles and binder, and then heating the shaped mixture at the liquidus temperature of the glass of the glass particles for a time sufficient for the glass particles to crystallise across the boundaries of contacting glass particles.

* See back of page

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METHOD OF MANUFACTURING GLASS-CERAMIC ARTICLES

This invention relates to a method of manufacturing glass-ceramic articles and to the articles made by the method.

It is well known that glass-ceramic products may be made by producing a molten glass from glass-forming constituents, or pieces of glass, which include a nucleating agent, forming the molten glass into a desired shape, for example by pressing into slabs, and then re-heating the formed glass shape at a temperature at which crystallisation occurs.

However the products obtained in this way always tend to have round edges as a result of the surface tension effect in the molten glass. Also it is difficult to form thin products and very difficult if not impossible to form a thin product having sharp corners.

Hitherto it has been thought that, when making a glass-ceramic article from discrete pieces of glass, it is necessary first to heat the glass particles to the melting temperature of the glass.

I have now made the surprising discovery that a glass-ceramic article may be produced by adhering together particles of powdered glass using a binder, and then heating the glass particle/binder mixture at the liquidus temperature of the glass, i.e. the

temperature at which, when a molten mass of that glass is cooled, the first crystals will appear. In the method of my invention, however, the solid glass particles are heated to the liquidus temperature, while the particles are held in contact with one another, so that maximum crystallisation of the glass will occur, in accordance with my invention, across the boundaries of the contacting glass particles. The glass particles should not be heated significantly above the liquidus temperature of the glass, in particular they must not be heated to a temperature near the softening temperature, because at such temperature the definite shape of a pressed glass-ceramic article will be lost.

In accordance with the present invention therefore there is provided a method of manufacturing glass-ceramic articles comprising the steps of mixing powdered glass particles with a binder, forming the mixture of powdered glass particles and binder into the shape of a desired article, and heating the shaped mixture at the liquidus temperature of the glass of the glass particles for a time sufficient for the glass particles to crystallise across the boundaries of contacting glass particles and thereby produce a glass-ceramic article of the desired shape.

By use of the method of the present invention, exact shapes can be made uninhibited by the tend ncy of molten glass to form round dges. In addition the

method enables a thinner product to b made than was possible by prior art processes and, in particular, the method in accordance with the present invention enables the production of thin products with sharp corners.

Preferably the powdered glass particles are of a size to pass an 850 micron sieve although smaller particle sizes may be used. The finer the powder used, the more dense is the final product. However smaller particle sizes give rise to shrinkage so that the size of the final article is less than the size of the shaped mixture taken from the mould in which the mixture was shaped. It has been found that, when the method in accordance with the present invention is performed using glass particles of a size to pass a 250 micron sieve, the article shrinks in size by about 10% although the article retains its shape and sharp corners. For smaller particle sizes the degree of shrinkage increases and for particle sizes of the order of 10 microns the shaped mixture will shrink by about 30% in size, although the desired shape is retained. The final articles are, in all cases, glass-ceramic articles of considerable strength and of high resistance to abrasion.

The binder used may be an organic binder which is destroyed during the heat treatment.

The process in accordance with the present invention has particular application in forming glass-ceramic

articles from a glass frit and more specifically from glass frits containing heavy metals prepared as described in my published International Patent Application No. WO 90/09211.

In the said International Patent Application I have described a method of treating toxic waste resulting from the incineration of industrial or domestic refuse in order to render the material harmless by forming it into a glass without releasing volatilised heavy metals and heavy metal compounds into the atmosphere. However in order to prevent volatilisation of the heavy metals from the molten glass when the molten glass is removed from the furnace, the molten glass must be quenched as quickly as possible by pouring it into water within an enclosed space from which volatilised metals and heavy metal compounds cannot escape. A method and apparatus for achieving this is particularly described in my aforementioned International Patent Application, and the resulting product is a glass frit.

When subjected to the internationally accepted standard test for leaching of heavy metals, German D.E.V.S. 4, the glass frit was shown to be acceptable for use as a product.

Although this glass frit may be used as such in products, for example in concrete, as an aggregate, in road foundation, or as an asphalt filler, it is

desirable to have further outlets for this safe waste product which will be produced in very large quantiti s because of the large quantities of refuse which have to be incinerated in modern industrial countries.

The toxic waste resulting from incineration of industrial or domestic refuse includes nucleating agents which are consequently also present in the glass frit product of the aforementioned International Patent Application. This glass frit product may be re-melted in a conventional cold-top furnace and fed via a forehearth to production machines for making the glass into tiles and pipes which are then re-heated to crystallise the glass. These crystallised glasses or slags are then more resistant to abrasion, chemical attack and leaching. They are also strong materials which are not subject to fracture in the way that normal glass products may fracture.

In accordance with the invention of the present application, the said glass frits are, as a further alternative, used as a raw material in forming glass-ceramic articles by a method in which powdered glass particles are caused to crystallise together at their points of contact by heating at the liquidus temperature of the glass.

The present invention will be further understood from the following detailed description.

Glass frit obtained from toxic waste by the method of my published International Patent Application No. WO 90/09211 is crushed to a powder. This powder is treated by a magnet to remove all free iron. Because the toxic wastes used in the method of the said co-pending patent applications usually contain carbon and other reducing agents as well as iron oxides, free iron metal and alloys are produced during melting. While some of this free metal lies on the bottom of the melter and is extracted therefrom, other free metal will be carried into the frit and it is this free metal which must be removed by a magnet.

The powder is then screened to a desired particle size and the screened powder is mixed with a binder to enable it to hold a shape prior to and during firing. The binder may be either an organic binder such as ethanol, starch, lignates or isopropanol, or an inorganic binder such as aluminium chloride, a phosphate or ethylsilicate. After mixing with binder the powder/binder mixture is shaped by any conventional method, such as machine pressing, rolling, vacuum forming or extrusion, and the shaped powder/binder mixture is then heat treated to form a solid product by heating to the liquidus temperature for the glass composition, usually a maximum temperature of the order of 1100°C - 1150°C, and holding the shaped mixture at this temperature for a period of the order of two hours so that a crystalline structure

is fully develop d by crystallisation across the contacting boundaries of the particles of the glass powder.

Because there are a variety of sources for the toxic waste treated by the method of my aforementioned International Patent Application, the glass frits derived therefrom have varying compositions. However, the glass frits derived from different sources are conveniently put into large heaps from which blended material of approximate known chemical composition may be extracted.

Glass frits were prepared by the method of my said International Patent Application from three batch compositions as follows:-

	1	2	3
Toxic Waste Fly Ash	40 pts	21 pts	40 pts
Limestone	50 pts	-	15 pts
Magnesite (Mg O)	4 pts	4 pts	40 pts
Power Station Fly Ash (P.F.A.)	100 pts	20 pts	100 pts
Sand (SiO_2)	-	20 pts	-
Residual Lime after Gas Washing		35 pts	-

Advantageously most ingredients of the batch compositions are themselves waste products, for example the magnesite may be obtained from the steel industry and the sand may be waste from grinding processes.

The three glass frits, which had melting

temperatures of the order of 1350°C, were then each divided into three separate samples and one of each of the three samples was treated by each of the three following processes:

Process A

The particles were crushed and sieved to extract all particles not passing an 850 micron sieve, the screened particles were mixed with a binder which was aluminium chloride or isopropanol, the particle/binder mixture was machine pressed under a pressure of 100 tons to produce a desired shape and the shaped mixture was fired at 1120°C (the liquidus temperature) for two hours. All three compositions were found to maintain their original shape and size, no shrinkage of the shaped mixture being evident after firing.

Process B

This process was the same as Process A except that the powdered frit was screened using a 250 micron sieve and only particles passing the 250 micron sieve were mixed with the aluminium chloride or isopropanol binder. After firing, all three compositions retained their shape and sharp corners but shrank by about 10%.

Process C

This was the same as Process A except that the powdered frits were screened using a 10 micron sieve and the particles passing the 10 micron sieve were mixed with isopropanol as binder. Again all three compositions

were found to retain their original shape but they all shrank by about 30%.

The products of all these processes were very dense glass-ceramic products with high resistance to abrasion and high strength.

In all the processes described, glass crystals have grown across the boundaries of contacting glass particles at a temperature below both the melting temperature and the softening temperature of the glass. The growth of crystals in this way at the liquidus temperature of the glass is a very surprising achievement.

Products made by the process of the present invention easily pass the D.E.V.S. 4 test for acceptability against leaching.

CLAIMS:

1. A method of manufacturing glass-ceramic articles comprising the steps of mixing powdered glass particles with a binder, forming the mixture of powdered glass particles and binder into the shape of the desired article, and heating the shaped mixture at the liquidus temperature of the glass of the glass particles for a time sufficient for the glass particles to crystallise across the boundaries of contacting glass particles and thereby produce a glass-ceramic article of the desired shape.

2. A method according to Claim 1 wherein the powdered glass particles are derived from a glass frit containing heavy metals.

3. A method according to Claim 1 or Claim 2 wherein the powdered glass particles are mixed with an inorganic binder.

4. A method according to Claim 1 or Claim 2 wherein the powdered glass particles are mixed with an organic binder.

5. A method according to any one of the preceding claims wherein the shaped mixture of powdered glass

particles and binder is heated at a temperature of the order of 1100°C for a period of two hours.

6. A method according to Claim 5 wherein the shaped mixture is heated at a temperature of 1120°C.

7. Glass-ceramic articles prepared by a method in accordance with any one of the preceding Claims.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01374

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 03 B 32/02, C 03 C 10/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 03 B; C 03 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 3942966 (KRØYER ET AL) 9 March 1976, see column 2, line 29 - line 39; column 3, line 12 - line 21 --	1,3,7
X	DE, A1, 3701973 (MATSUSHITA ELECTRIC WORKS, LTD) 30 July 1987, see column 5, line 30 - line 37; column 6, line 41 - line 45 --	1,4,7
X	Patent Abstracts of Japan, Vol 12, No 132, C490, abstract of JP 62-252341, publ 1987-11-04 (MATSUSHITA ELECTRIC WORKS LTD) --	1,7

* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10th December 1990	19. 12. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. Peis / M. PEIS

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 3450546 (GUY E. STONG) 17 June 1969, see the whole document	1-7

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 90/01374

SA 40273

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent ffice EDP file on 01/11/90
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 3942966	09/03/76	AU-D-	5479673	24/10/74
		BE-A-	798446	16/08/73
		CA-A-	980367	23/12/75
		CH-A-	580549	15/10/76
		DE-A-	2320471	08/11/73
		FR-A-	2186447	11/01/74
		GB-A-	1402757	13/08/75
		JP-A-	49022408	27/02/74
		NL-A-	7305450	23/10/73
		SE-B-C-	385467	05/07/76
DE-A1- 3701973	30/07/87	JP-A-	62171943	28/07/87
		US-A-	4764486	16/08/88
		JP-A-	62216939	24/09/87
US-A- 3450546	17/06/69	FR-A-	1528167	00/00/00

For more details about this annex : see fficial Journal of the European patent Office, No. 12/82

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